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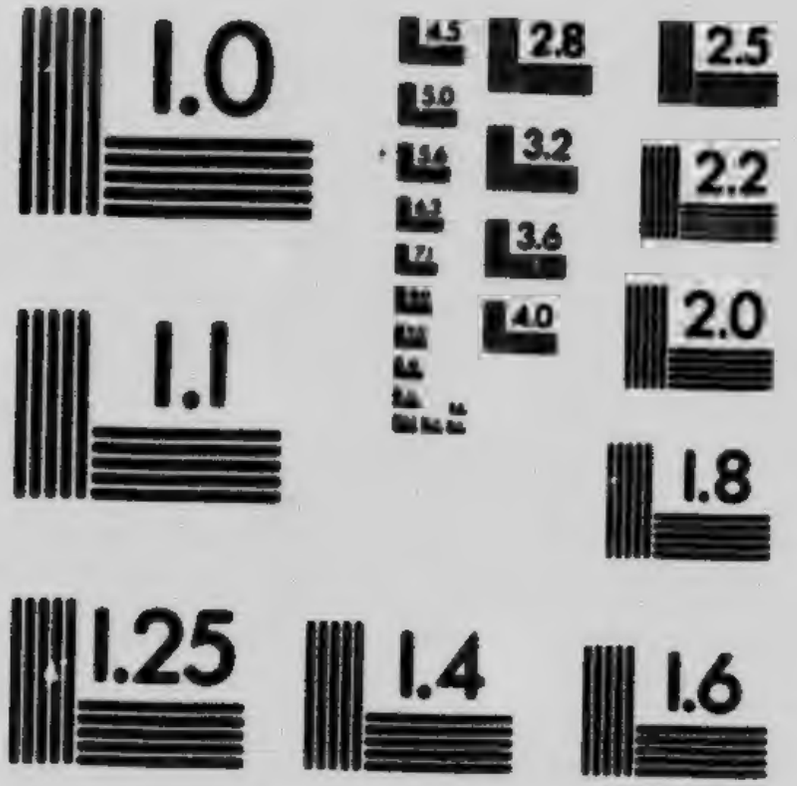

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THE INFLUENCE OF DIFFUSION ON ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS BY CENTRIFUGAL ACTION.

By W. Lash Miller.

In reading Tolman's account of his measurements of the electromotive force produced in solutions by centrifugal action,[1] I noticed that the equations for the electromotive force were deduced without allowing for any possible differences in concentration at the two ends of the tube produced by the whirling, as in some of his experiments these differences would become very considerable if the rotation were sufficiently prolonged, it seemed possible that even in a few minutes the "concentration cell" effect might become measurable, and that it might perhaps account for the "residual electromotive force" observed by him.

The calculations carried out in the following paragraphs show, however, that the polarization produced by concentration changes in short periods of centrifuging is very slight. During the rotation both iodine and iodide keep increasing in concentration at the outer electrode and decreasing at the inner, but the E.M.F. that would be produced by an increase of one percent in the concentration of the iodine alone is almost counterbalanced by a rise of one-third percent in the concentration of the iodide; and, as will be shown, the iodine concentration rises, at first, just about three times as rapidly as that of the iodide; so that the E.M.F. actually generated is very small, much too small to account for the "residual" voltage observed by Tolman.

As, so far as I am aware, no attempts have hitherto been made to calculate the rate at which diffusion would take place under the influence of centrifugal force, a short account of the method which I have adopted may prove of interest. Briefly stated, it consists (*1*) in determining the distribution of concentrations along

[1] Proc. Am. Acad. Arts and Sci., **46**, 109 (1910). Jour. Am. Chem. Soc.

[2] Acad., *loc. cit.* p. 116, foot note.

the tube when equilibrium has been reached (*i. e.*, when the solution has been whirled for an "infinite" time) by the usual thermodynamic method; (*2*) in treating this equilibrium as due to the equality of two "virtual" rates of flow, one (towards the axis) due to concentration gradient, and the other (toward the periphery) due to centrifugal force; (*3*) in expressing the former of these by Fick's equation for the rate of diffusion along a fall of concentration, and thus (*4*) finding a plausible expression for the second or virtual flow due to centrifugal force. Assuming, then, that the actual flow at any moment is represented by the algebraical sum of the two components, expressions for which have thus been obtained, (*5*) a differential equation is set up, and a solution obtained to suit the conditions of Tolman's experiments.

The method just described is employed in calculating the rate of diffusion of the potassium iodide in solutions originally normal with regard to the iodide and fiftieth normal with regard to free iodine, the effect of the small quantity of iodine on the diffusion of the iodide being neglected. In calculating the rate of diffusion of the iodine in the same solutions, however, it had to be remembered that, in the absence of centrifugal force and of iodine-concentration difference, iodine will diffuse from a dilute to a concentrated solution of potassium iodide. This fact, which is taken account of in the present system of chemical formulas by distinguishing between "dissolved I_2" and "$\overline{I_2}$," is here allowed for by introducing a third "virtual flow," that due to iodide-concentration difference, as explained below.

POTASSIUM IODIDE, CONCENTRATIONS AT EQUILIBRIUM.

The distribution of concentration along the centrifugal tube when equilibrium is reached is given by the expression

$$\mu - \frac{2\,\pi^2 N^2\,(1-vd)\,x^2}{981 \times 42660} = const. \qquad (1)$$

where μ is Gibbs' thermodynamic potential; it may be replaced by

$$\frac{1.980}{F}\ log\ nat\ z + const.$$

[N is the number of revolutions of the axis per second; θ the thermodynamic temperature, 293 in Tolman's experiments; F the thermodynamic

formula weight, assuming 78 percent dissociation $F = 166/1.78$; z is the concentration of the iodide, as only ratios occur in the formulas, any units will do; v the "partial volume" (Tolman) of the iodide $= 0.284$; d, the density of the solution, $= 1.115$; $\pi = 3.1416$; the divisor 981×42660 converts ergs to calories; 1.98 is the gas constant.]

whence, neglecting the change of vd with the concentration,

$$[at\ equil.]\ z = Ae^{\beta x^2}\ ;\ where\ \beta = 5.180 \times 10^{-8} N^2 \quad (2)$$

Since the total amount of iodide in the tube remains constant,

$$\int_r^R z\,dx = z_0(R - r);\ whence\ A = z_0(R - r) \Big/ \int_r^R e^{\beta x^2}\,dx \quad (3)$$

[z_0 is the initial concentration of the iodide, uniform throughout the tube, (normal, in Tolman's work); r (Tolman's r_1) the distance of the inner electrode from the axis, and R (Tolman's r_2) that of the outer electrode, both in centimeters. As the outer electrode fitted the end of the tube and the inner electrode had almost the same cross section as the tube, r and R give the distance of the effective inner and outer ends of the column of solution from the axis. In the experiments with potassium iodide and iodine, $r = 4.3$ and $R = 29.40$]

The definite integral on the right may be evaluated by expanding $e^{\beta x^2}$ and integrating term by term. When $N = 82$ (the greatest speed in the potassium iodide experiments), $\beta = 3.484 \times 10^{-4}$ and $A = 0.898\ z_0$; hence when equilibrium is attained at a speed of 82 revolutions per second, the concentration of the iodide at the outer electrode will be 1.213 normal, and at the inner will be 0.904 normal, a ratio of 1.34 to 1.00.

POTASSIUM IODIDE, RATE OF DIFFUSION.

If the motor were stopped after the state of equilibrium had been attained, there would immediately ensue a flow of salt through the solution away from the peripheral end of the tube, the amount of which is given by

$$Concentration\ now\ towards\ axis = k\frac{\partial z}{\partial x} \quad (4)$$

where k is the diffusion constant (cm^2, sec) of potassium iodide at 20° C. in normal or approximately normal solution. I have taken $k = 1.45 \times 10^{-5}$.

As explained above, this "concentration flow" may be regarded

as just balanced, at equilibrium, by the "centrifugal flow" in the opposite direction; the latter would therefore be represented by

$$\textit{Centrifugal flow toward axis} = -k\frac{\partial z}{\partial x}\textit{at equil.,} = -2k\beta xz \qquad (5)$$

Thus an expression for the centrifugal flow at equilibrium is obtained, and it is assumed that (5) will hold whatever the distribution of concentrations; *i. e.*, that in general

$$\textit{Flow towards axis} = k\frac{\partial z}{\partial x} - 2k\beta xz \qquad (6)$$

When the motor is first started, $\frac{\partial z}{\partial x}$ will be zero, and the "flow" will be negative, *i. e.*, the salt will move towards the outer end of the tube; when equilibrium is attained the flow will be zero; and when the motor is stopped β will be zero, and the flow will become positive in sign, *i. e.*, the salt will move towards the axis.

The *accumulation* at any point of the tube, x cm. from the axis, will then be given by

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x} - 2k\beta xz\right) \qquad (7)$$

which is the differential equation sought. It is subject to the conditions that, as no salt can enter or leave the tube, the "flow" at $x=r$ and $x=R$ must be zero, or

$$[\textit{at } x=r \textit{ and } x=R]\ k\frac{\partial z}{\partial x} - 2k\beta xz = 0 \qquad (8)$$

and, moreover, that at the beginning of the experiment the concentration has the uniform value z_0 throughout the tube, *i. e.*,

$$[\textit{at } t = 0]\ z = z_0 \textit{ for all values of } x \textit{ from } r \textit{ to } R \qquad (9)$$

A solution of (7) that will satisfy (8) and (9) will therefore give the concentration at any point of the tube at any moment after rotation has begun.

Such a solution can be arrived at by means of successive approximations; for the present purpose, however, the problem may be simplified by neglecting the very slight variations in the centrifugal flow caused by the slight changes in concentration

which occurred along the tube in Tolman's experiments. Equations (7) and (8) then become.

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial z}{\partial x} - 2k\beta x z_0\right) \qquad (10)$$

$$[at\ x=r\ and\ x=R]\cdot k\frac{\partial z}{\partial x} qz - \beta x z_0 = 0 \qquad (11)$$

while equation (9) remains as before.

These three equations, viz., (9), (10) and (11), are satisfied by

$$\frac{z-z_0}{\beta z_0} = \frac{4l^2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2}\cdot\cos\frac{n\pi(x-r)}{l}\cdot e^{-\frac{n^2\pi^2 kt}{l^2}} +$$

$$\frac{8lr}{\pi^3}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\cdot\cos\frac{(2n-1)\pi(x-r)}{l}\cdot e^{-\frac{(2n-1)^2\pi^2 kt}{l^2}}$$

$$-(r^2+rl+\frac{l^2}{3})+x^2 \qquad (12)^*$$

Replacing y by $\pi(x-r)/l$ in the cosine series

$$y^2 = \frac{\pi^2}{3} - 4\sum\frac{(-1)^{n+1}}{n^2}\cos ny$$

and $$y = \frac{\pi^2}{2} - \frac{4}{\pi}\sum\frac{1}{(2n-1)^2}\cos(2n-1)y$$

(given, for example, in Byerly's "Fourier's Series and Spherical Harmonics," pages 44 and 45), there results

$$x^2 = r^2 + rl + \frac{l^2}{3} - \frac{4l^2}{\pi^2}\sum\frac{(-1)^{n+1}}{n^2}\cos\frac{n\pi(x-r)}{l}$$

$$-\frac{8rl}{\pi^2}\sum\frac{1}{(2n-1)^2}\cdot\cos\frac{(2n-1)\pi(x-r)}{l}$$

whence, for small values of kt/l^2 such as occur in Tolman's experiments,

$$[for\ x=r]\ \frac{z}{z_0} - 1 = -\frac{4R+8r}{3l\sqrt{\pi}}\beta\sqrt{kt} \qquad (13)$$

$$[for\ x=R]\ \frac{z}{z_0} - 1 = \frac{8R+4r}{3l\sqrt{\pi}}\beta\sqrt{kt} \qquad (14)$$

*In (12) l is written as a contraction for $R \pm r$.

In a paper by T. R. Rosebrugh and W. Lash Miller (Jour. Phys. Chem. 14, 826 (1911) equation 21) it is shown that for small values of at

$$\sum_{n=1}^{\infty} \frac{1}{p} e^{-p^2 at} = \frac{\pi^2}{8} - \frac{1}{2}\sqrt{\pi at}, \text{ approximately}$$

where $p = 2n-1$. From this it may be deducted that when $p = 2n$, the series is approximately equal to $\frac{\pi^2}{24} - \frac{1}{6}\sqrt{\pi at}$.)

As β is proportional to N^2, it follows from (13) and (14) that the time needed to bring about any given small change in concentration at either end of the tube is inversely proportional to the fourth power of the rate of rotation. What is ordinarily considered a rapid centrifuge, running at 2,000 revolutions per minute, would take over half an hour to accomplish what Tolman's apparatus (82 rev. per sec.) did in one minute.

IODINE, CONCENTRATIONS AT EQUILIBRIUM.

In dilute solutions of iodine in normal potassium iodide (where, in the language of the theory of solutions, practically all the free iodine is present as $\overline{I_3}$ or KI_3)

$$[\textit{free iodine}]\ \mu = \textit{const.} + \frac{\cdot\cdot 98\theta}{254}\ \textit{log nat}\ \frac{w}{z}$$

where w is the concentration of the iodine (*i. e.*, of the total free iodine determinable by thiosulphate) and z that of the potassium iodide. Introducing this value of μ into equation (1), and neglecting the change of vd with the concentration, there results

$$[\textit{at equil.}]\ \frac{w}{z} = Be^{\gamma x}\ ;\ \textit{where}\ \gamma = 15.18 \times 10^{-8} N^2 \quad (15)$$

[For dilute solutions of iodine in potassium iodide solution Tolman finds $v = 0.2376$; $d = 1.115$ as before.]

Replacing z by its value from (2) gives

$$[\textit{at equil.}]\ w = ABe^{(\beta + \gamma)x^2} \quad (16)$$

in which AB can be determined as A was in (3).

When $N = 82$, $\beta = 3.484 \times 10^{-4}$, $\gamma = 10.21 \times 10^{-4}$, $AB = 0.6345$; thus when equilibrium has been attained at a speed of

82 revolutions per second, the concentration of the free iodine at the outer electrode will be 0.0414 normal ($z_0 = 0.02$ normal), and that at the inner electrode 0.0130 normal, a ratio of 3.18 to 1.00.

IODINE, RATE OF DIFFUSION.

Regarding the flow of free iodine through the solution (towards the axis reckoned positive) as made up of three components, the first of these, that due to differences in iodine concentration, may be set

$$Iodine\text{-}concentration\ component = K\frac{\partial w}{\partial x} \qquad (17)$$

[Brunner's experiments (Zeit. phys. Chem. **58** 22-28 (1907)) seem to show that K is about $\frac{2}{3}\ k = 9.7 \times 10^{-6}$; two direct measurements made here by Mr. Pirie, gave 10.4×10^{-6} and 11.6×10^{-6}. In the computations 10×10^{-6} is used.]

where K is the diffusion constant of free iodine in approximately normal potassium iodide. The second, due to centrifugal force, may be set (as in equation 5)

$$Centrifugal\ component = -2K\gamma x w \qquad (18)$$

the third is then determined, since at equilibrium the total flow is zero,

$$Iodide\text{-}concentration\ component = 2K\gamma x w - K\frac{\partial w}{\partial x}\ at\ equil.$$

$$= -K\frac{w}{z}\frac{\partial z}{\partial x} \qquad (19)$$

The differential equation for the free iodine is therefore

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial w}{\partial x} - 2K\gamma x w - K\frac{w}{z}\frac{\partial z}{\partial x}\right) \qquad (20)$$

the boundary and initial conditions being

$$(at\ x = r\ and\ x = R)\ \frac{\partial w}{\partial x} - 2\gamma x w - \frac{w}{z}\frac{\partial z}{\partial x} = 0 \qquad (21)$$

$$[at\ t = 0]\ w = w_0\ for\ all\ values\ of\ x\ from\ r\ to\ R \qquad (22)$$

A solution which fits the conditions of Tolman's experiments

may be obtained by writing z_0 for z in (20) and (21) and replacing $\frac{\partial z}{\partial x}$ by its value from (12), viz., $2\beta z_0 x$. Equation (20) then becomes

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial w}{\partial x} - 2K(\beta + \gamma)xw\right) \qquad (23)$$

which is the same in form as (7). Expressions for w at $x=r$ and at $x=R$ valid for small values of Kt/l^2 may therefore be obtained by substituting K for k, w for z, and $\beta+\gamma$ for β in (13) and (14).

ELECTROMOTIVE FORCE OF THE CONCENTRATION CELL.

The net result of passing a current of electricity through the tube, so that the outer electrode is cathode, is that for every 96,540 coulombs 127 grams free iodine are lost at the outer electrode and gained at the inner, and 0.486 × 166 grams* of potassium iodide are gained at the outer and lost at the inner electrode. Writing Z_R, Z_r for the concentrations of the potassium iodide at the outer and inner electrodes respectively, W_R and W_r for those of the free iodine, and assuming that the iodide is 78 percent dissociated, the E.M.F. at 20° C. due to the concentration difference will be

$$E.M.F. = 0.000099 \times 293 \times \log_{10}\frac{W_R Z_r}{W_r Z_R} - 0.000198 \times 293 \times 0.486 \times 1.78 \times \log_{10}\frac{Z_R}{Z_r} \text{ volts} \qquad (24)$$

$$= 0.0126 \log \text{nat}\frac{W_R}{W_r} - 0.0344 \log \text{nat}\frac{Z_R}{Z_r} \text{ volts.} \qquad (25)$$

When the difference between Z_R and z_0 does not exceed one percent or so, $\log \text{nat } Z_R$ may be replaced by the right hand member of equation (14), and similarly with the other logarithms; this gives

$$E.M.F. = (R + r)(0.0284\beta + \gamma\sqrt{Kt} - 0.0776\beta\sqrt{kt}) \qquad (26)$$

or, inserting the values of R, r, β, γ, K and k

$$E.M.F. = 1.034 \times 10^{-10} N^2 \sqrt{t} \text{ volts} \qquad (27)$$

*0.486 is the transport number of the cation in potassium iodide solution.

The following table gives the gain or loss at each electrode in percents of the initial concentration, and the resulting E.M.F. in millivolts, for Tolman's three experiments with potassium iodide and iodine; on the assumption that in each case the salt was evenly distributed throughout the solution before rotation began.

N	t Sec.	Iodine		Iodide		E. M. F. Millivolts
		Inner Percent	Outer Percent	Inner Percent	Outer Percent	
62	150	— 0.087	+ 0.144	— 0.025	+ 0.021	0.0049
76	210	— 0.154	+ 0.256	— 0.044	+ 0.074	0.0087
82	60	— 0.096	+ 0.159	— 0.028	+ 0.046	0.0054

After running for fifteen minutes at 82 rev. per sec there would be a difference of one percent between the concentrations of the iodine at the two electrodes; but even then, owing to the simultaneous changes in concentration of the iodide, the E.M.F. would not reach 0.021 millivolt.

The University of Toronto,
February, 1912.